

A Practical Approach for the Preparation of Regioregular Poly(3-hexylthiophene)

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Received June 11, 2009, Accepted November 9, 2009

Key Words: Regioregularity, Organozinc, Poly 3-hexylthiophene, Polythiophenes

Polythiophenes have been intensively studied over the last three decades. And major studies have been focused on poly 3-alkylthiophene especially poly 3-hexylthiophene (P3HT), which has shown very unique properties in conducting polymer applications. Of these, the most notable property is electrical conductivity, which is contributed to the delocalization of π -electrons through overlap of π -orbitals. In addition to this, since it is very soluble in normal organic solvents, a good processability has been observed.

In general, preparation of P3HT could be achieved by either chemical or electrochemical method. For electrochemical polymerization including FeCl_3 catalyzed polymerization, a potential was applied to a solution containing monomer and electrolyte.² Chemical synthesis was performed by metal-mediated polymerization of monohalogenated and/or dihalogenated thiophene derivatives under appropriate conditions.³ An advantage in chemical polymerization over electrochemical method is that this method generally affords a highly regioregular polymer in excellent yields.

Since regioregularity of P3HT is a critical element for the application of this polymer, a lot of different procedures have been developed especially in chemical synthetic methods. Generally accepted methods include metal (Ni) catalyzed self-condensation of thienyl organozinc and thienyl Grignard reagents. A big breakthrough for the preparation of regioregular P3HT has been reported by Rieke⁴ and McCullough,⁵ separately. From these works, high regioregular (> 98%) head-to-tail P3HT has been achieved with reasonable molecular weight.

As mentioned above, 2,5-dibromo-3-alkylthiophenes have been extensively used as a monomer in the chemical synthetic method. However, only a few examples of using 2-bromo-5-iodo-3-alkylthiophenes have been appeared in the chemical method.⁶

Recently, Knochel and co-workers⁷ introduced the application of commercially available and relative cheap zinc powder to organic synthesis. This work prompted us immediately to study the possibility of using zinc powder in the preparation of

P3HT. To this end, 2-bromo-5-iodo-3-alkylthiophene could be the most proper candidate since zinc dust showed excellent insertion reactivity to carbon-iodine bond.

Here, we wish to report the first result obtained from the application of the activated zinc dust to the preparation of regioregular P3HT.

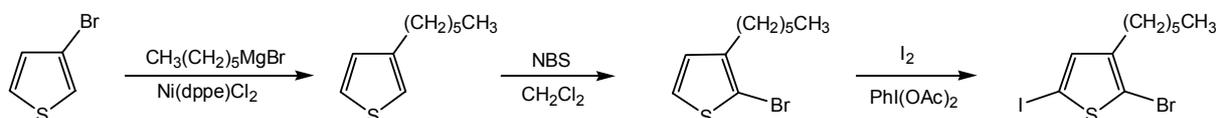
Results and Discussion**Preparation of monomer (2-bromo-3-hexyl-5-iodothiophene).**

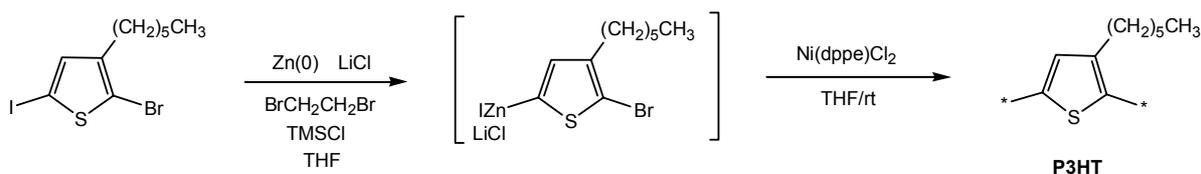
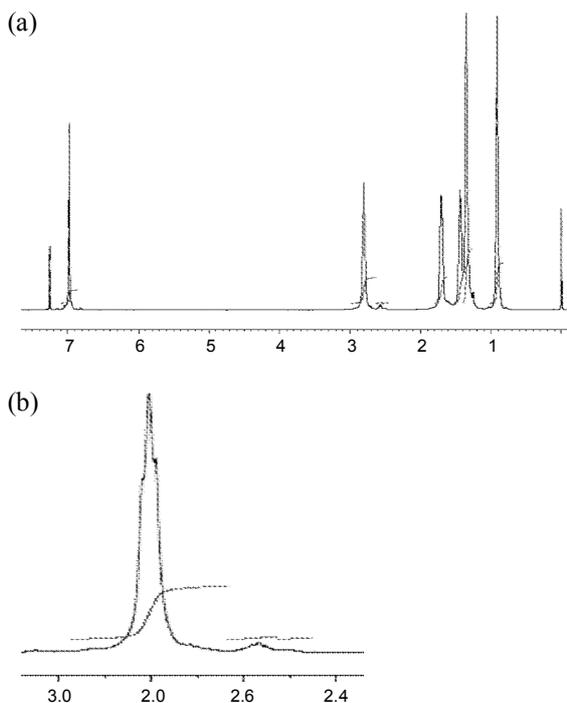
There are several reports on the synthesis of 2-bromo-5-iodo-3-alkylthiophenes.⁸ As described in Scheme 1, alkyl substituent on thiophene ring was easily introduced by utilizing the coupling reaction of Grignard reagent with 3-bromothiophene in the presence of Ni-catalyst. Selective bromination on 2-position of the thiophene ring is the key step and successfully accomplished by using NBS under the conditions shown in Scheme 1. Iodination of the resulting monobrominated thiophene was easily carried out using iodine and $\text{PhI}(\text{OAc})_2$ under mild conditions affording 2-bromo-3-hexyl-5-iodothiophene in 60% overall yield.

Preparation of regioregular poly 3-hexylthiophene (P3HT).

In 1992, it was reported that the highly active zinc underwent the direct oxidative addition to 2,5-dibromo-3-alkylthiophenes chemoselectively to afford 2-bromo-5-bromozincio-3-alkylthiophenes.⁴ The resulting organozinc was used for Ni-catalyzed polymerization to make high regioregular poly 3-alkylthiophenes. Since almost the same intermediate could be obtained from the oxidative addition of zinc dust to 2-bromo-3-hexyl-5-iodothiophene, it is very optimistic to make high regioregular poly 3-hexylthiophene. A simple schematic diagram is described in Scheme 2.

Of interest, oxidative addition of the activated zinc dust⁷ to 2-bromo-3-hexyl-5-iodothiophene in the presence of lithium chloride was easily accomplished at room temperature in THF and showed excellent chemoselectivity. Acidic aqueous quenching of the resulting organozinc solution, followed by GC-MS

**Scheme 1.** Preparation of monomer

**Scheme 2.** Preparation of P3HT**Figure 1.** ^1H NMR spectra (a: full, b: methylene region).

analysis, confirmed the exclusive formation (> 98%) of 2-bromo-3-hexylthiophene, which is the corresponding compound of 2-bromo-5-iodozincio-3-hexylthiophenes. In order to exploit other possible use of this condition, more attempts were tried. Unfortunately, no conversion to organozinc was observed from utilizing 2,5-dibromo-3-hexylthiophene under the same conditions used in this study. And also, treatment of 2-bromo-3-hexyl-5-iodothiophene with the zinc dust in the absence of lithium chloride resulted in low conversion (< 20%).

With the resulting organozinc in hand, polymerization was carried out to prepare P3HT. As described in the previous reports,⁴ the catalyst choice was critical in determining the regio-regularity in the resultant polymer. Therefore, in this study, Ni(dppe)Cl₂ was the first candidate for the polymerization and executed in good manner. Other catalysts such as Ni[P(Ph)₃]₂Cl₂, Ni[P(Me)₃]₂Cl₂, Fe(dppe)Cl₂, and Co(dppe)Cl₂ were tried but polymerization was failed.

Polymerization was easily completed at room temperature in 24 h. A catalytic amounts of Ni(dppe)Cl₂ was added into the organozinc solution through a powder funnel while being stirred at rt. Upon the addition of the catalyst, the reaction mixture usually turned a dark solution, and the formation of polymer was observed in a few minutes. To complete the polymerization, the resulting reaction mixture was allowed to stir at rt for 24 h.

A general work up and purification gave the title polymer in 80% isolated yield. Soxhlation with hexanes over 24 h gave pure head-to-tail poly(3-hexylthiophene). Since the regio-regularity of P3HT has been determined by ^1H NMR,⁴ it was accomplished with P3HT prepared in this study. As shown in Figure 1, only one sharp band in the aromatic region as well as a clean triplet in the methylene region of the ^1H NMR spectrum have been observed. The expanded ^1H NMR spectrum in the α -methylene proton region was indicative of > 96% for the regioregular linkage. In the ^{13}C NMR spectrum, only four sharp bands for the thiophene carbon atoms were observed.⁹ A reasonable molecular weight (Mw = 28000, determined by gel permeation chromatography, THF eluent, relative to polystyrene standard) and PDI (1.98) have been obtained. An additional Soxhlet extraction with chloroform after the hexanes treatment has shown a better regioregularity (> 98%). However, no significant improvement was observed in molecular weight.

Despite the relatively low molecular and high PDI,⁹ this method has clearly shown another practical synthetic route for the preparation of high regioregular P3HT of using an easily assessable zinc powder.¹⁰

In conclusion, we have demonstrated the synthesis of regioregular poly 3-hexylthiophene mediated by zinc powder, which is relatively cheap and commercially available, under mild conditions. This procedure could be applied to the synthesis of other regioregular poly 3-alkylthiophenes. Further studies on this reaction are currently underway.

Experimental Section

Preparation of 2-bromo-3-hexyl-5-iodothiophene. Prepared by a literature procedure.⁸

Polymerization. Anhydrous zinc dust (4.5 g, 70 mmol, 325 mesh, Strem) and lithium chloride (2.1 g, 50 mmol) were weighted out from the Dry-Box. Then the flask was dried under high vacuum pressure at 160 ~ 170 °C for 20 min and recharged with Ar-gas. This procedure was repeated twice. Next, 50 mL of THF was added, followed by addition of 1,2-dibromoethane (5 mol %) and Me₃SiCl (1 mol %). With being stirred at rt, 2-bromo-3-hexyl-5-iodothiophene (18.5 g, 50 mmol) was added neat into the flask. The insertion was completed in 2 h at rt (confirmed by GC analysis of reaction aliquot showing > 98% selectivity, quantitative conversion). Settling down the reaction mixture gave two phases. The supernatant was cannulated into a 250 mL flask and then 0.08 g of Ni(dppe)Cl₂ (0.3 mol %) was added into the reaction mixture through a powder funnel. The resulting mixture was stirred at rt for 24 h. Then, the whole mixture was poured into methanol affording a black polymer. Filtered and washed with methanol, then dried under high vacuum. Soxhlet extraction with hexanes for

24 h gave 6.6 g (80% isolated yield) of regioregular poly 3-hexylthiophene.

General procedure for Soxhlet extraction with chloroform.

The polymer previously extracted with hexanes was placed in a Soxhlet extractor and then extracted with chloroform for 12 h. The resulting chloroform solution was then poured slowly into MeOH while being stirred at rt. Polymer was precipitated and then filtered, washed with MeOH, and then dried under high vacuum pressure affording the regioregular P3HT as a black solid. Generally, polymer is recovered more than 90%.

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9. For the representative data; $M_w = 37680$, PDI = 1.49 from Rieke's work,⁴ $M_n = 17000$, PDI = 1.28 from Yokozawa's work,⁸ $M_n = 20000 - 35000$, PDI = 1.20 - 1.47 from McCullough's work.^{5b}
10. For the representative methods; the Rieke method⁴ requires the preparation of Rieke zinc *via* alkali metal reduction of zinc chloride, and the McCullough method⁵ requires cryogenic and/or refluxing temperatures.